DEFECT ANNEALING IN IRRADIATED SEMICONDUCTORS

NASA RESEARCH GRANT NsG - 602

PROGRESS REPORT

OCTOBER 1, 1965 to MARCH 31, 1966

By

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April 1, 1966

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INTRODUCTION

This report describes progress for the period October 1, 1965 to March 31, 1966 in the research program supported by NASA Research Grant NsG - 602.

Research work in this period involved:

1. Calculation of empirical values of isothermal annealing model parameters.
2. Determination of the best theoretical fit of experimental isothermal annealing data given by approximate solutions of the annealing equations.
3. Calculation of activation energies for vacancy motion from the empirical annealing model parameters.

There was one publication during the report period:

"Vacancy Activation Energy in n - Type Germanium" by W. Maurice Pritchard, Bulletin of the American Physical Society, Series II, Vol 11, No. 2, 1966.

EMPIRICAL MODEL PARAMETERS

It has been shown (1) that for the special case in which the break-up rate for secondary defect complexes is zero, the solution of the annealing equation is

$$\frac{1}{K_1 i_o} \int_p^1 \frac{dp}{p\left[p + \frac{I_o}{i_o}\left(p^{K_2/K_1} - 1\right)\right]} = t \qquad (1)$$

where

$p = \frac{i}{i_o}$ = fraction of defects not annealed

i_o = initial concentration of interstitial atoms

I_o = initial concentration of impurity atoms

K_1 = rate constant for annihilation of vacancies

K_2 = rate constant for trapping of vacancies by impurity atoms

t = time after start of isothermal annealing

The equation for the annealing plateau level p = p, obtained by setting $\frac{dp}{dt} = 0$, is

$$P + \frac{I_o}{i_o} (P^{K_2/K_1} - 1) = 0 \qquad (2)$$

Since the ratio $\frac{I_o}{i_o}$ is known with reasonable accuracy, equation (2) can be used to determine values of $\frac{K_2}{K_1}$ required to give the experimental plateau levels.

Solving equation (2) for K_2/K_1 yields

$$\frac{K_2}{K_1} = \frac{\ln (1 - \frac{i_o}{I_o} P)}{\ln P} \qquad (3)$$

Table I shows the required K_2/K_1 values for the isothermal annealing data of Pigg and Crawford (2) obtained with antimony doped n - type germanium. Table II lists K_2/K_1 values for the data of Brown, Augustyniak, and Waite (3) on antimony doped n - type germanium.

Table I

Annealing Temperature	Plateau P	$\frac{K_2}{K_1}$
377.2 ^oK	0.520	0.3128
407	0.430	0.1965
410	0.300	0.1529
425.5	0.274	0.0793
455	0.230	0.0583

Table II

307 ^oK	0.32	0.1530
313	0.29	0.1266
329	0.26	0.1035
349	0.25	0.0990
370	0.23	0.0832

For the Table I data, $\frac{I_o}{i_o} = 2.81$ and for Table II, $\frac{I_o}{i_o} = 2.00$.

An examination of the required K_2/K_1 values indicates that $\frac{K_2}{K_1}$ must be of the order of 0.1. In addition, $\frac{K_2}{K_1}$ appears to be a monotonic decreasing function of annealing temperature for both sets of data. Theoretical considerations of the diamond lattice structure (5) indicate that the number of ways in which a vacancy can arrive at an annihilation site or impurity trapping site are the same. The fact that K_2/K_1 must be of the order of 0.1 indicates that the trapping cross section must be about an order of magnitude smaller than the annihilation cross section.

BEST THEORETICAL FIT OF ANNEALING DATA

If $\frac{I_o}{i_o}$ is known and $\frac{K_2}{K_1}$ is assigned an empirical value as previously described, the integral

$$G(p) = \int_p^1 \frac{dp}{p\left[p + \frac{I_o}{i_o}\left(p^{K_2/K_1} - 1\right)\right]} \tag{4}$$

can be evaluated numerically. A computer program was written to perform this integration by Simpson's Rule. The isothermal annealing equation (1) then becomes

$$G(p) = K_1 i_o\, t \tag{5}$$

The constant $K_1 i_o$ can be evaluated by a weighted least squares technique to give the best overall fit of equation (5) to experimental isothermal annealing data. The least squares equation for $K_1 i_o$ is

$$K_1 i_o = \frac{\sum_{i=1}^{N} W_{G_i}\, G_i t_i}{\sum_{i=1}^{N} W_{G_i}\, t_i^2} \tag{6}$$

where

$G_i = G(p_i)$

$p_i = p(t_i)$

W_{G_i} = weighting factor for G_i

According to Deming (4), the ratio of weighting factors for G and p values is

$$\frac{W_G}{W_p} = \frac{\sigma_p^2}{\sigma_G^2} = \left| \frac{1}{\frac{\partial G}{\partial p}} \right|^2 \tag{7}$$

where σ^2 is the standard deviation. From equation (4)

$$\frac{\partial G}{\partial p} = - \frac{1}{p\left[p + \frac{I_o}{i_o} (p^{K_2/K_1} - 1)\right]}$$

so that

$$\frac{W_G}{W_p} = p^2\left[p + \frac{I_o}{i_o} (p^{K_2/K_1} - 1)\right]^2 \tag{8}$$

If the errors in p measurements are normally distributed,

$$W_p = \frac{1}{\sigma_p^2} \tag{9}$$

and

$$W_{G_i} = \frac{p_i^2}{\sigma_{p_i}^2} \left[p_i + \frac{I_o}{i_o} (p_i^{K_2/K_1} - 1)\right]^2 \tag{10}$$

The p_i values must be presumed to be measured with the same accuracy; for lack of any information to the contrary. Therefore, $\sigma_{p_i}^2$ has the same value for all p_i. In this case, equation (6) becomes

$$K_1 i_o = \frac{\sum_{i=1}^{N} p_i^2\left[p_i + \frac{I_o}{i_o} (p_i^{K_2/K_1} - 1)\right]^2 G_i t_i}{\sum_{i=1}^{N} p_i^2 \left[p_i + \frac{I_o}{i_o} (p_i^{K_2/K_1} - 1)\right]^2 t_i^2} \tag{11}$$

A computer program was written to first calculate $K_1 i_o$ from equation (11) and then calculate t as a function of p from equation (5). This procedure was used to determine the best empirical fit of the annealing model to two sets of experimental isothermal annealing data for n - type germanium. Figures 1 - 5 show the best theoretical curves and the experimental curves obtained by Pigg and Crawford (2). Figures 6 - 10 are for the data of Brown, Augustyniak, and Waite (3). The agreement between theoretical and experimental curves is generally good.

VACANCY ACTIVATION ENERGIES FOR GERMANIUM

The theoretical expression (5) for the rate constant K_1 is

$$K_1 = \gamma \bar{\nu} e^{-\frac{E}{KT}} \tag{12}$$

where

γ = 26 = Geometric Factor for Diamond Structure

$\bar{\nu}$ = 0.572×10^{13} sec^{-1} = Average Lattice Frequency

K = Boltzmann Constant

E = Activation Energy for Vacancy Motion

T = Absolute Temperature

Solving equation (12) for E gives

$$E = K T L n \frac{\gamma \bar{\nu}}{K_1} \tag{13}$$

If equation (12) is in error by no more than one order of magnitude, the error in E can be estimated as

$$E = \pm K T L n (10). \tag{14}$$

Table III gives $K_1 i_o$ values obtained by the method of least squares, activation energies from equation (13) and estimated errors from equation (14) for the data of Pigg and Crawford (2). Table IV gives the same information for the data of Brown, Augustyniak, and Waite (3). The calculations for Table III were based on $i_o = 5 \times 10^{13} cm^{-3} = 1.10 \times 10^{9}$ atomic fraction and for Table IV,

$i_o = 1 \times 10^{15}$ cm^{-3} = 2.20×10^{-8} atomic fraction.

Table III

T (^oK)	$K_1 i_o$ (min^{-1})	E (ev)	ΔE (ev)
377.2	0.2618×10^{-3}	0.79	0.07
407	0.4529×10^{-2}	0.75	0.08
410	0.1146×10^{-1}	0.73	0.08
425.5	0.3059×10^{-1}	0.72	0.08
455	0.7606×10^{-1}	0.73	0.09

Table IV

T (^oK)	$K_1 i_o$ (sec^{-1})	E (ev)	ΔE (ev)
307	0.1522×10^{-3}	0.63	0.06
313	0.2641×10^{-3}	0.63	0.06
329	0.1116×10^{-2}	0.62	0.07
349	0.5490×10^{-2}	0.61	0.07
370	0.2430×10^{-1}	0.60	0.07

The average activation energy for the data of Pigg and Crawford (2) is

$$\bar{E} = 0.74 \pm 0.08 \text{ ev} \qquad (15)$$

For the data of Brown, Augustyniak, and Waite (3),

$$\bar{E} = 0.62 \pm 0.07 \text{ ev} \qquad (16)$$

In neither case does there appear to be a significant variation of E with annealing temperature.

Since both sets of data are for antimony doped n - type germanium, the results (15) and (16) are inconsistent. The value of E generally reported (3) as deduced from isochronal annealing experiments is E = 0.8 ev. This value is consistent with the value 0.74 ± 0.08 ev deduced from the isothermal annealing data of Pigg and Crawford (2). The value 0.62 ± 0.07 ev deduced from the

isothermal annealing data of Brown, Augustyniak, and Waite is much too low. This apparently indicates a lower accuracy in the data reported by these authors.

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3. Brown, W. L., W. M. Augustyniak, and J. R. Waite, J. Appl. Phys. 30, 1258 (1959).

4. Deming, Statistical Adjustment of Data, J. Wiley & Sons, Inc., New York, 1943, p. 22.

5. Pritchard, W. M., Defect Annealing in Irradiated Semiconductors, Progress Report No. 1, October 1, 1964, Old Dominion College, Norfolk, Virginia.

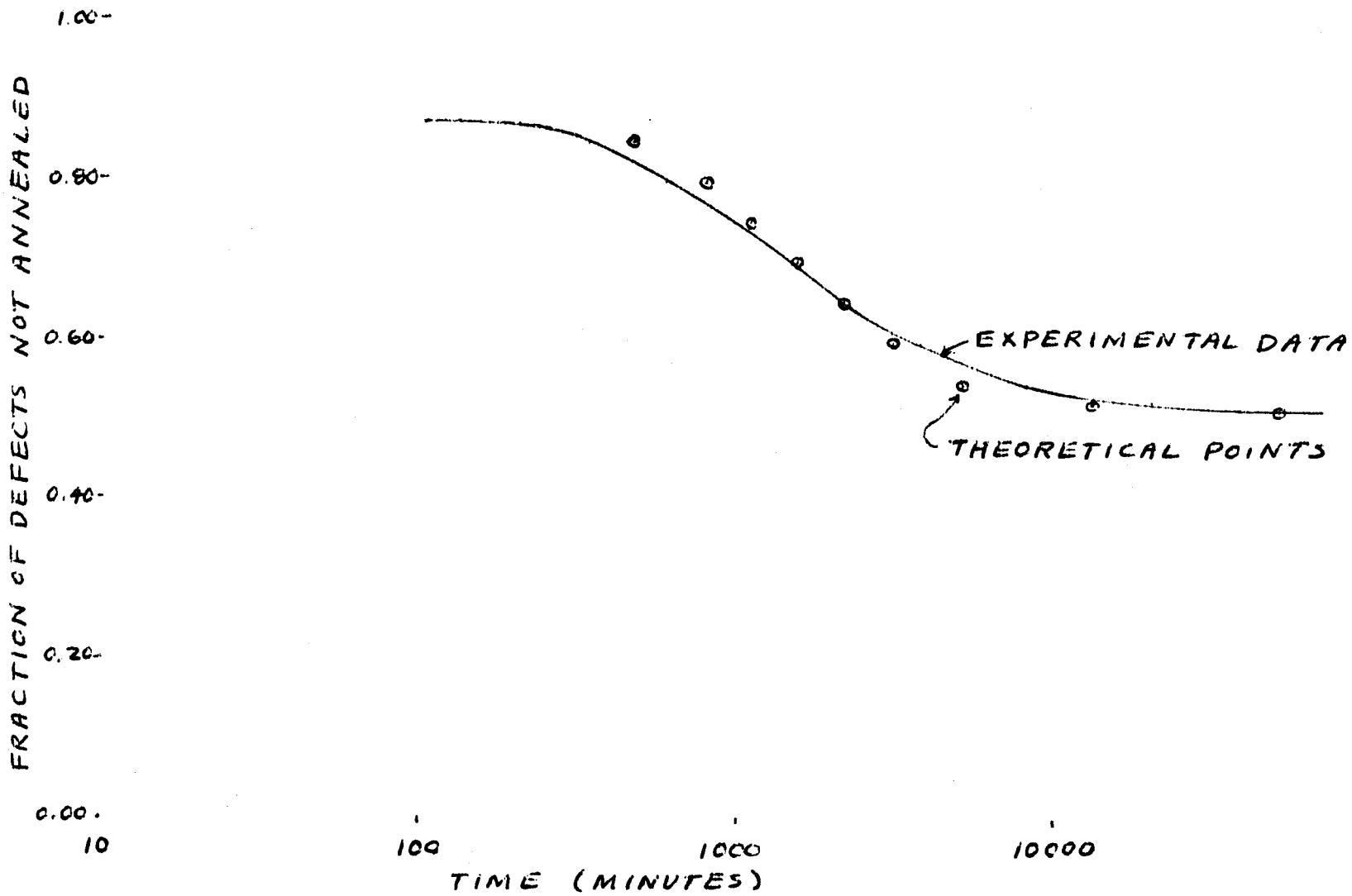

FIGURE 1. 377.2 °K P&C (2)

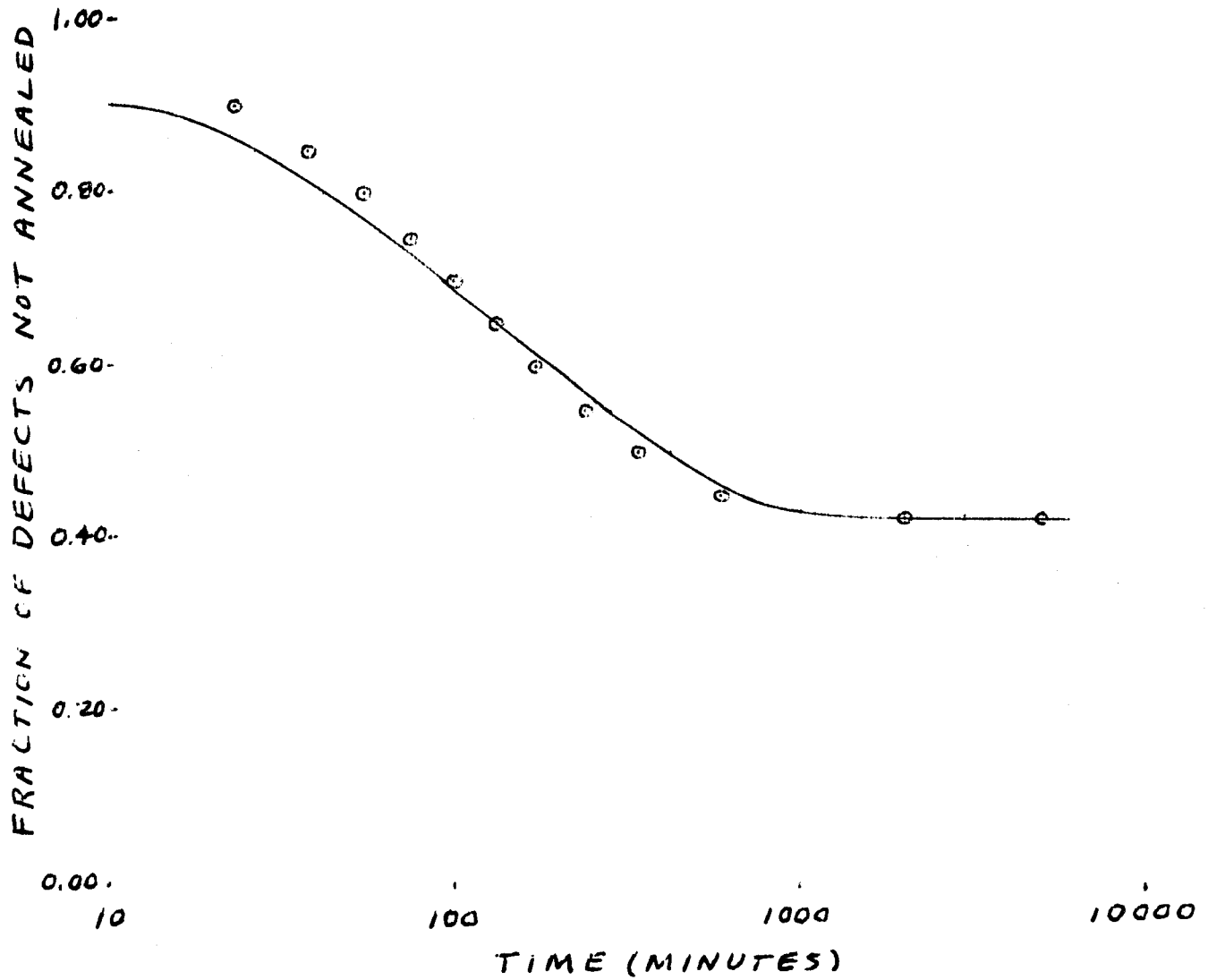

FIGURE 2. 407 °K P&C (2)

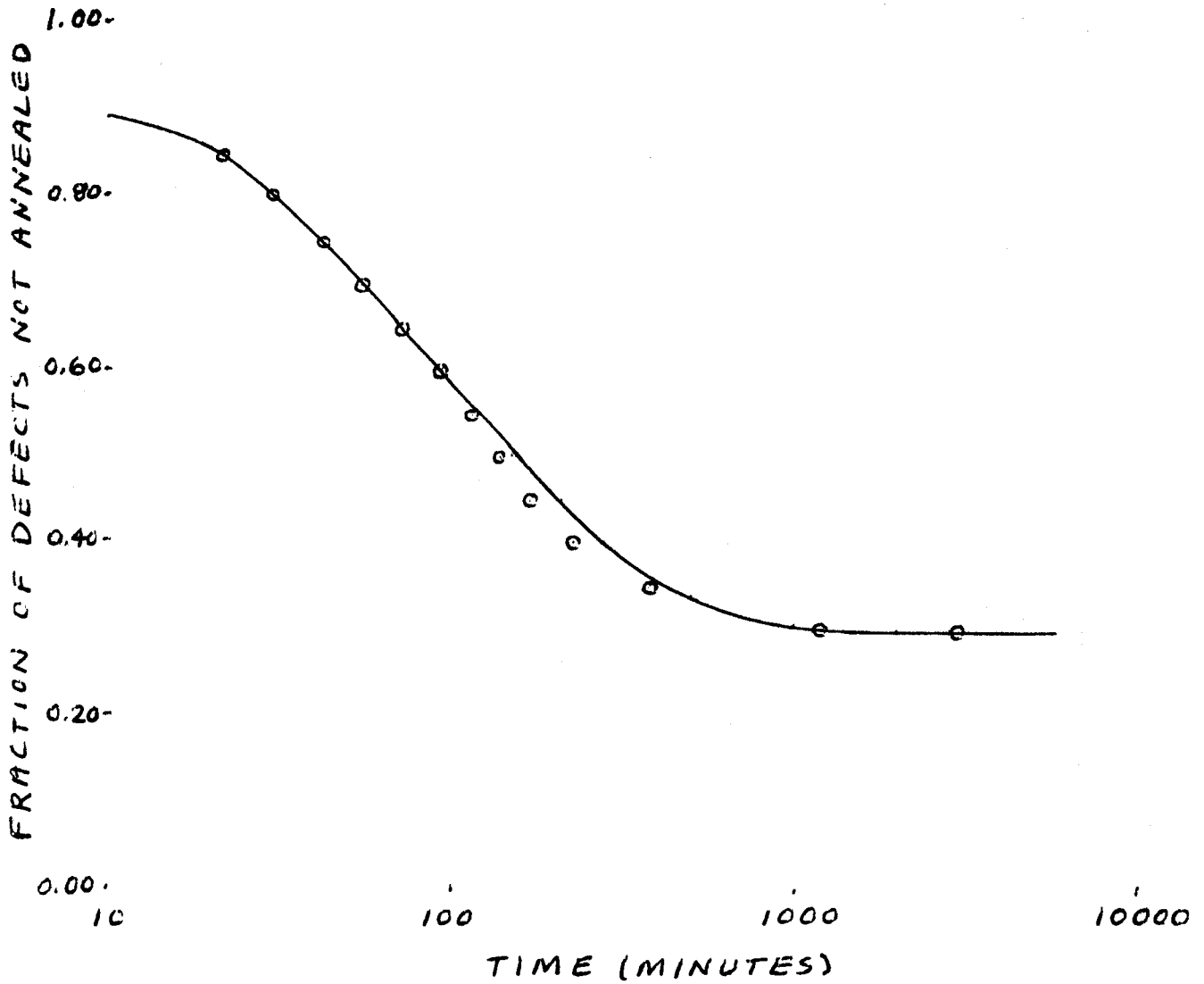

FIGURE 3. 410 °K P&C (2)

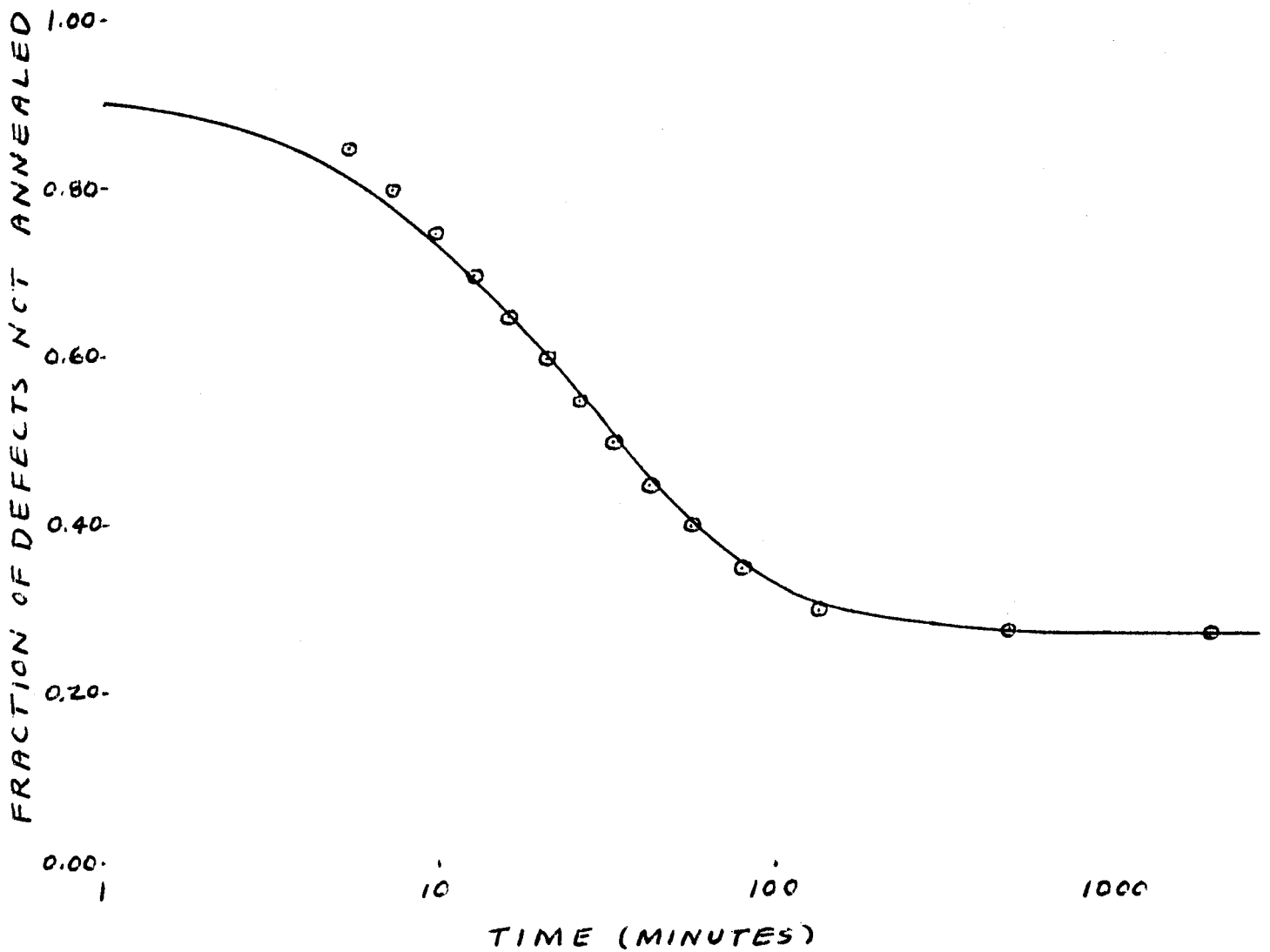

FIGURE 4. 425.5°K P&C (2)

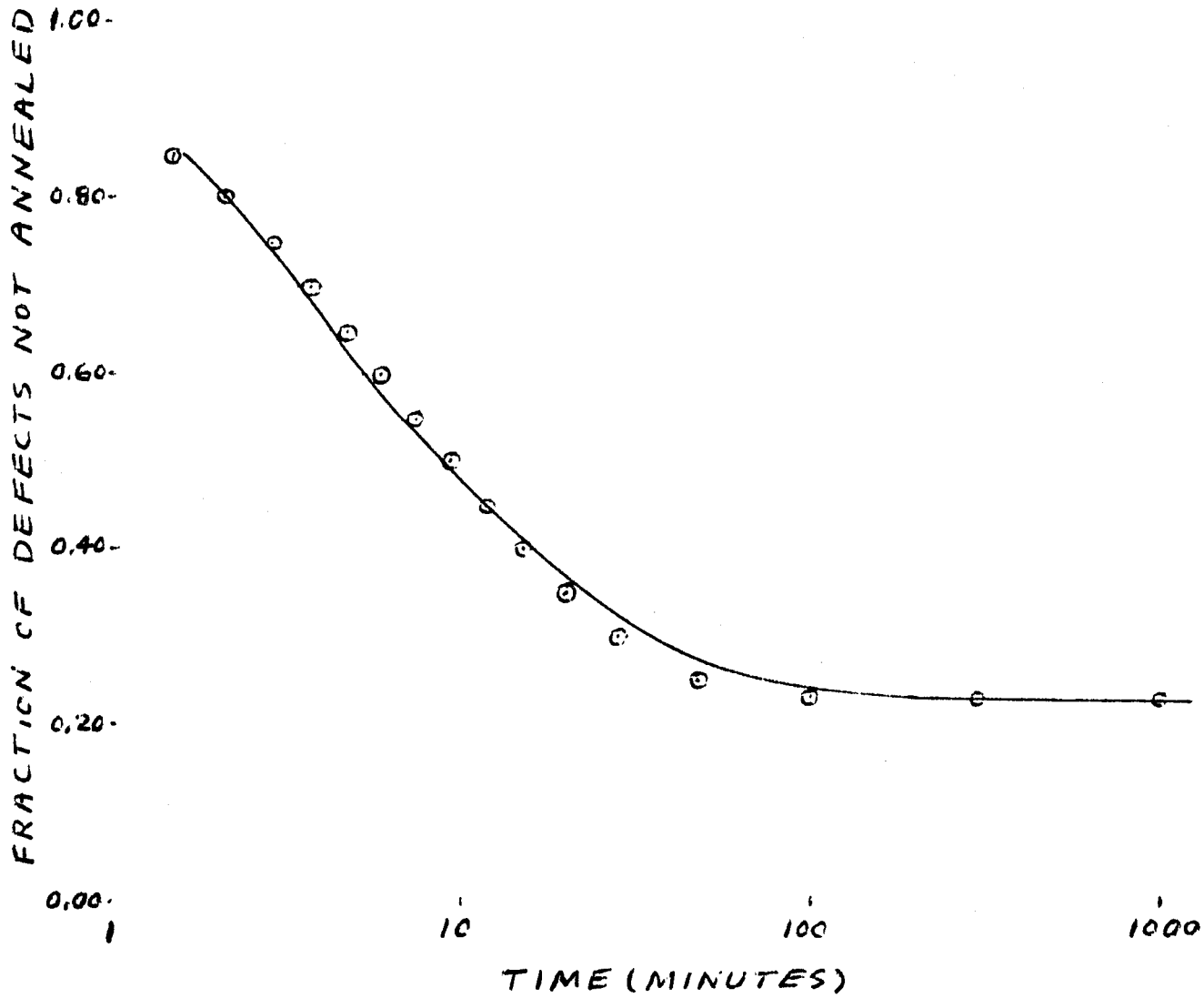

FIGURE 5, 455°K P&C (2)

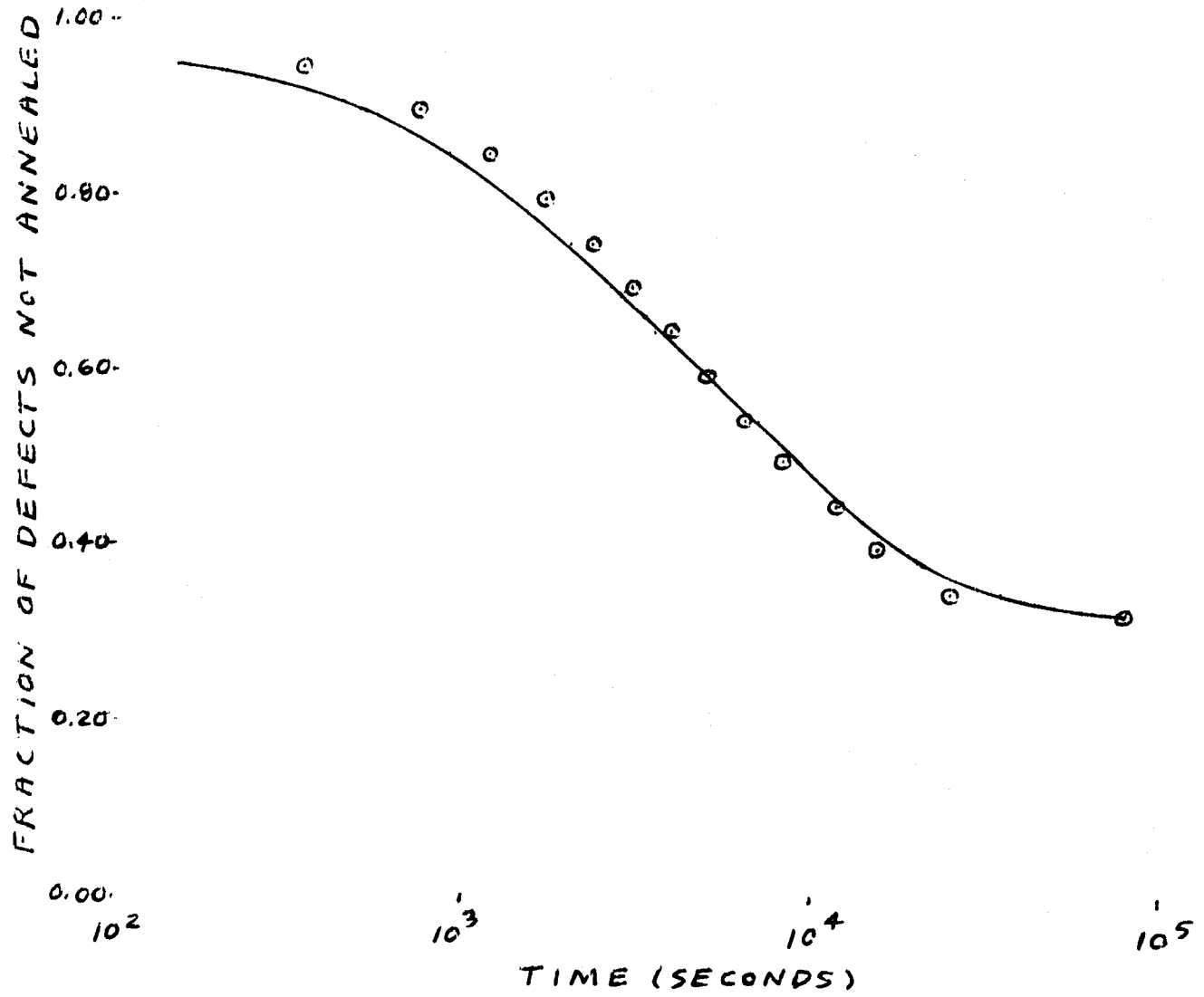

FIGURE 6. 307 °K BAW (3)

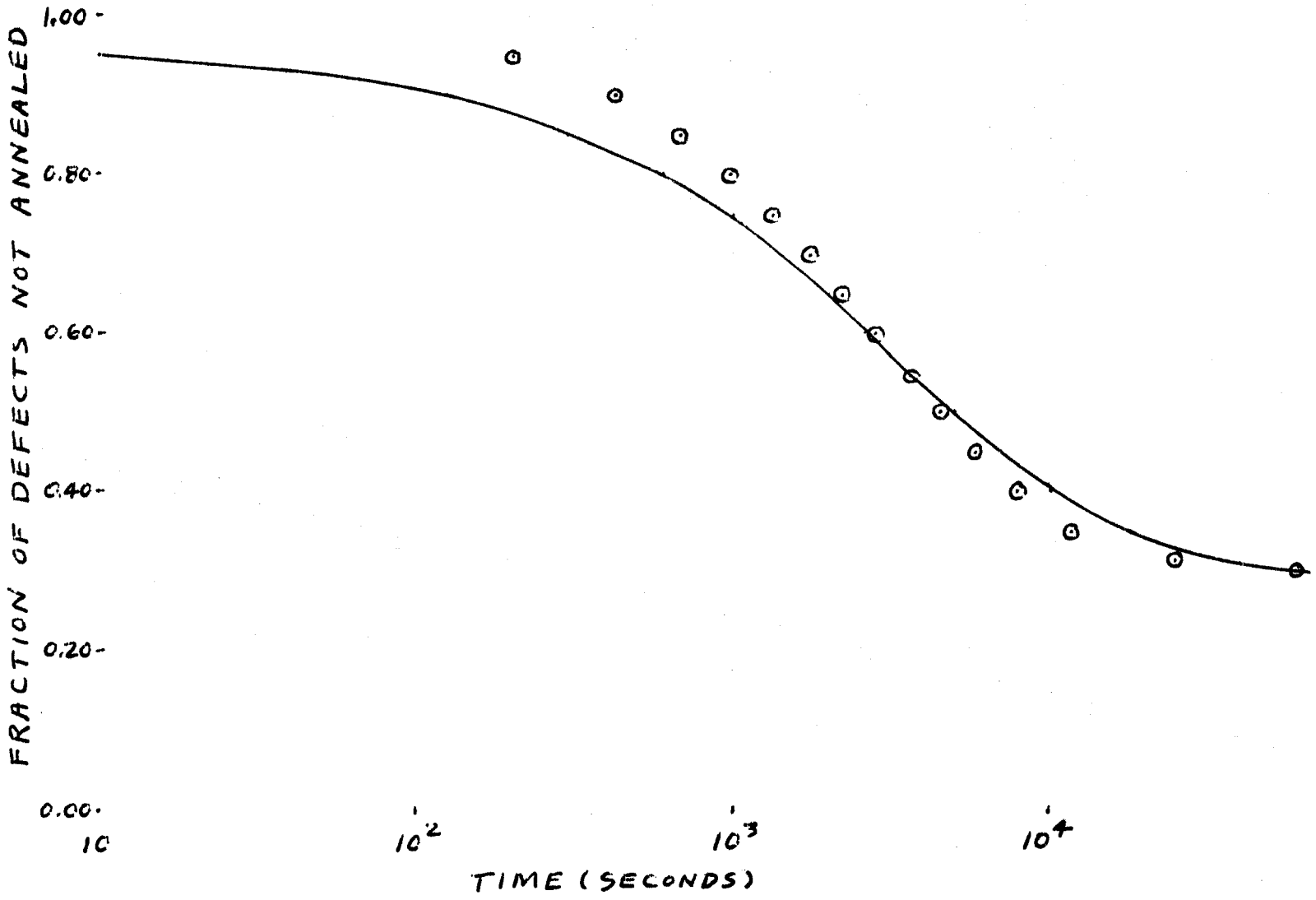

FIGURE 7. 313 °K BAW (3)

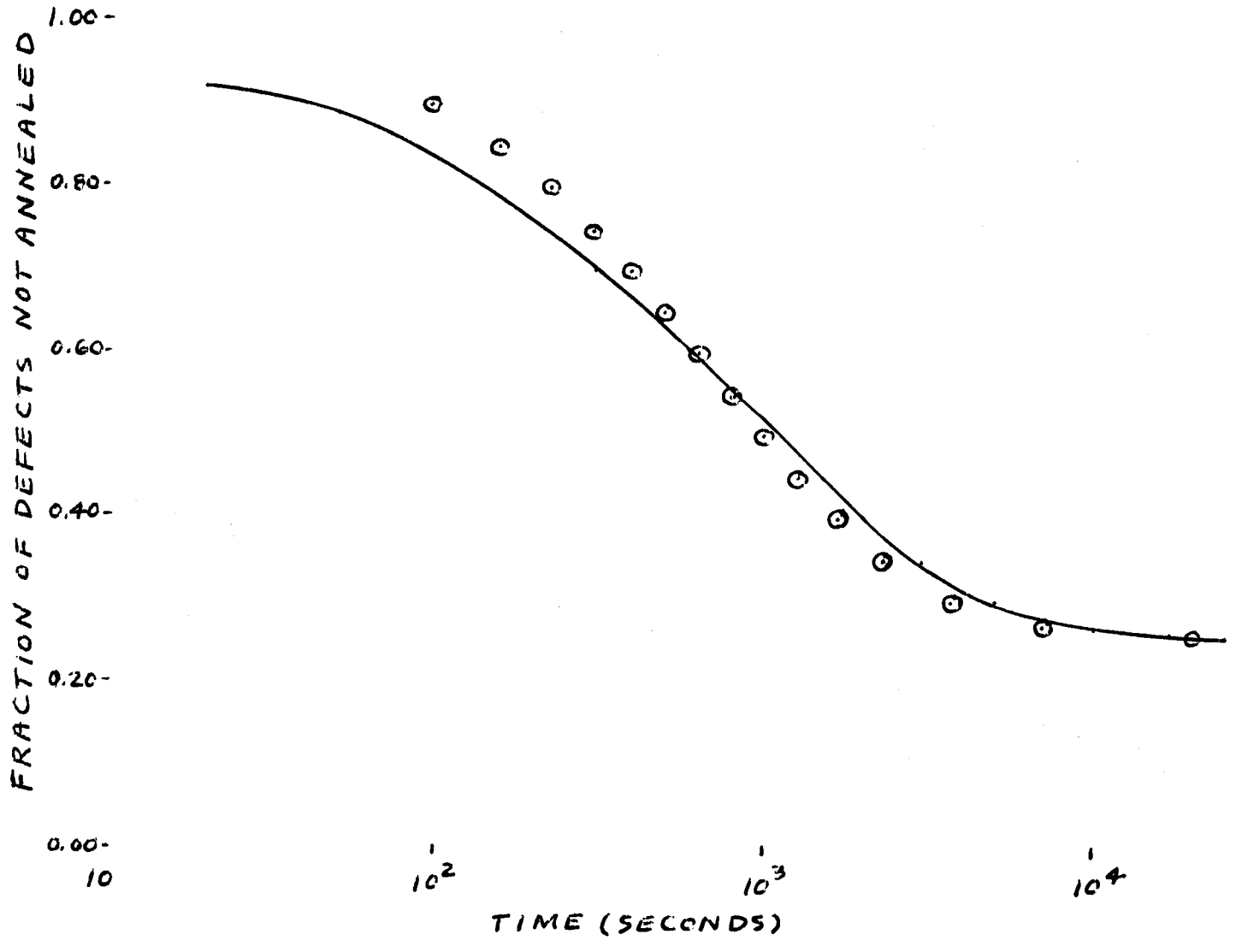

FIGURE 8 329 °K BAW (3)

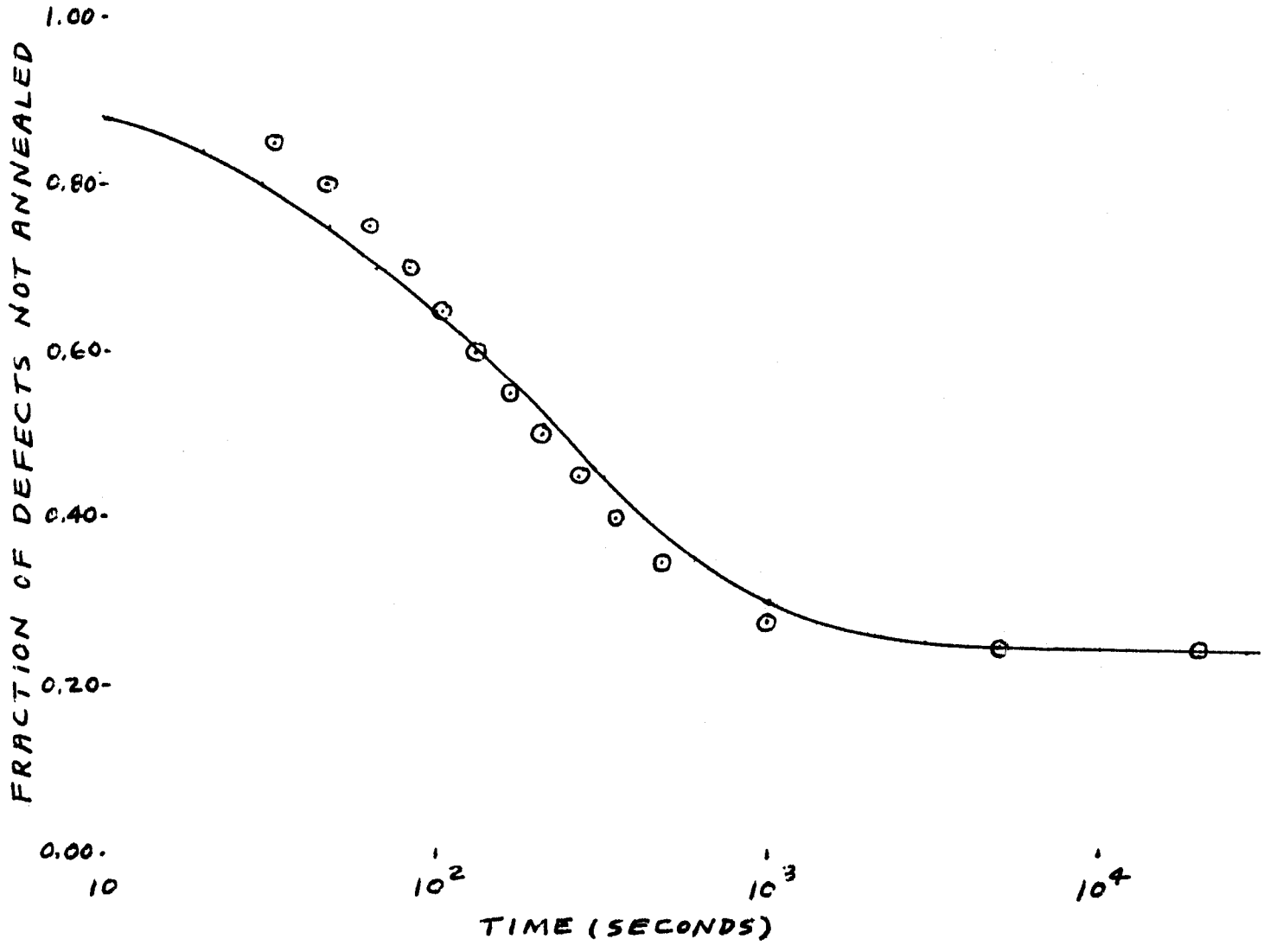

FIGURE 9, 349 °K BAW (3)

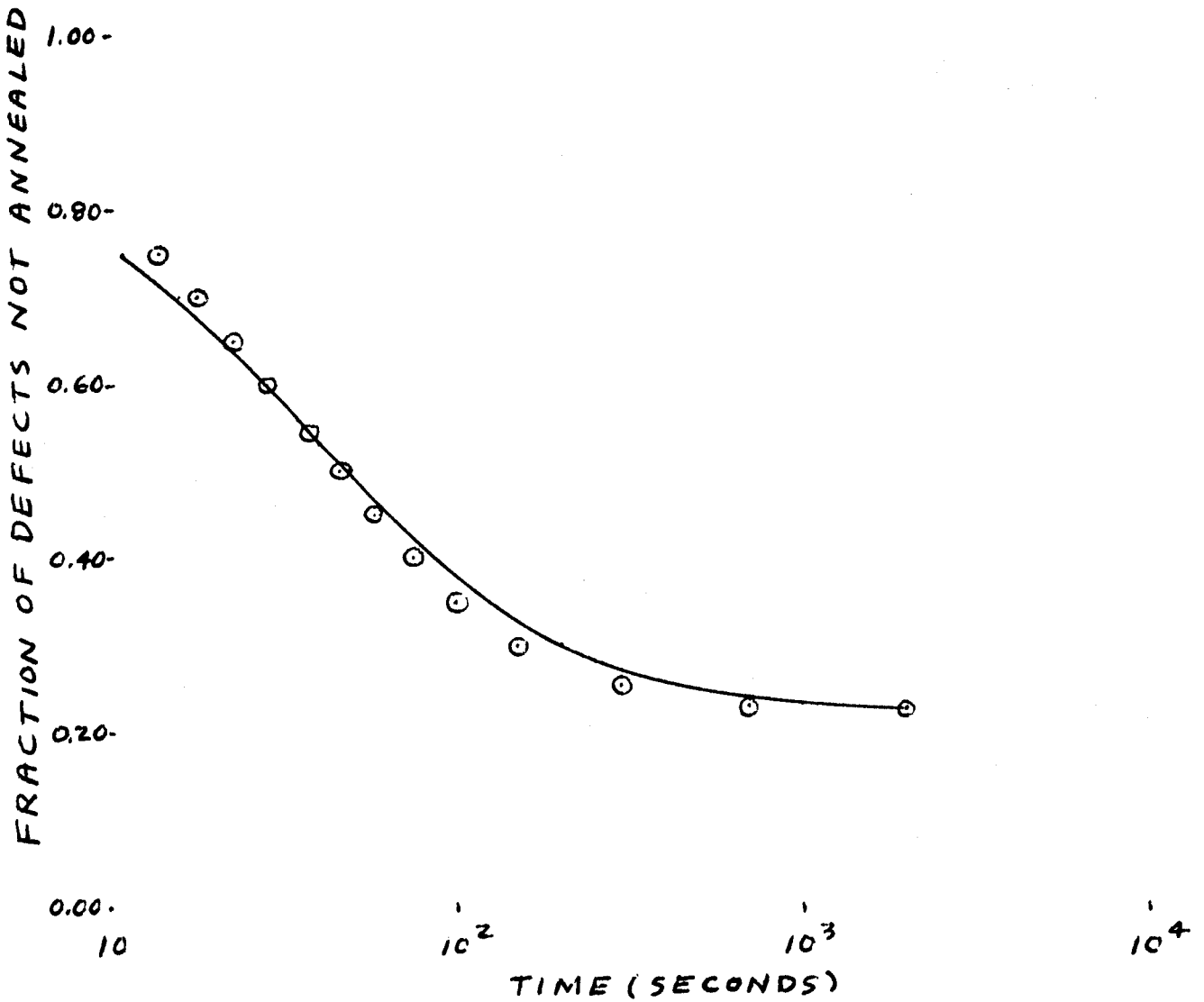

FIGURE 10. 370 °K BAW(3)